Diffusion and emissions of 1,3-dichloropropene in Florida sandy soil in microplots affected by soil moisture, organic matter, and plastic film

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Abstract: The main objective of this study was to determine the influence of soil moisture, organic matter amendment and plastic cover (a virtually impermeable film, VIF) on diffusion and emissions of (Z)and (E)-1,3-dichloropropene (1,3-D) in microplots of Florida sandy soil (Arredondo fine sand). Upward diffusion of the two isomers in the Arredondo soil without a plastic cover was greatly influenced by soil-water content and (Z)-1,3-D diffused faster than (E)-1,3-D. In less than 5 h after 1,3-D injection to 30 cm depth, (Z)- and (E)-1,3-D in air dry soil had diffused to a 10 cm depth, whereas diffusion for the two isomers was negligible in near-water-saturated soil, even 101h after injection. The diffusion rate of (Z)- and (E)-1,3-D in near-field-capacity soil was between the rates in the two water regimes. Yard waste compost (YWC) amendment greatly reduced diffusion of (Z)- and (E)-1,3-D, even in air-dry soil. Although upward diffusion of (Z)- and (E)-1,3-D in soil with VIF cover was slightly less than in the corresponding bare soil; the cover promoted retention of vapors of the two isomers in soil pore air in the shallow subsurface. More (Z)-1,3-D vapor was found initially in soil pore air than (E)-1,3-D although the difference declined thereafter. As a result of rapid upward movement in air-dry bare soil, (Z)- and (E)-1,3-D were rapidly volatilized into the atmosphere, but emissions from the near-water-saturated soil were minimal. Virtually impermeable film and YWC amendment retarded emissions. This study indicated that adequate soil water in this sandy soil is needed to prevent rapid emissions, but excess soil water slows diffusion of (Z)- and (E)-1,3-D. Thus, management for optimum water in soil is critical for pesticidal efficacy and the environment.

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Keywords: fumigant; 1,3-D; diffusion; emission; soil; microplot

1 INTRODUCTION

The fumigant 1,3-dichloropropene (1,3-D) is frequently mentioned as a potential replacement for methyl bromide, $^{1-8}$ the use of which will be suspended in January 2005. 9 1,3-Dichloropropene has very good pesticidal activity in controlling soil-borne phytoparasitic nematodes and, to some extent, fungal pathogens. 9 Unlike methyl bromide, which at $\geq 4\,^{\circ}$ C is a gas, 1,3-D at ambient temperature is a liquid with a boiling point $>100\,^{\circ}$ C. 10 This chemical consists of two stereoisomers, (Z) and (E). (Z)-1,3-D is more volatile than its counterpart (E)-1,3-D, 34.3 versus 23.0 mm Hg at 25 $^{\circ}$ C, but slightly less water

soluble than (E)-1,3-D, 2.18 versus 2.32 g liter⁻¹.¹⁰ 1,3-Dichloropropene in water and soil is not chemically stable, being subject to chemical hydrolysis and microbial degradation.^{11–13} Its hydrolysis rate in water depends on temperature, with half-life values of 11.3 and 3.1 days at 20 and 30 °C, respectively.¹²

In order for 1,3-D to render adequate pesticidal efficacy, sufficient 1,3-D concentration has to remain in the soil root-zone for an adequate length of time before escaping into the atmosphere or being degraded. To retard volatilization into the atmosphere, plastic films may be used to cover soil surface. Polyethylene film (PE) was found ineffective in

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retarding 1,3-D emissions. 14,15 Soil moisture and organic matter content may influence 1,3-D diffusion and volatilization in soil. An increase in organic matter content will increase sorption capacity and degradation of 1,3-D in soil, 16 resulting in lower 1,3-D concentration in soil pore air space. However, an increase in soil-water content will reduce available soil pore air space and retard 1,3-D diffusion and emissions. In this study, we determined the effects of soil moisture, soil organic matter and VIF plastic cover on diffusion and emissions of (Z)- and (E)-1,3-D in a Florida sandy soil under microplot environment.

2 MATERIALS AND METHODS

2.1 Materials and microplots

The (Z)- and (E)-1,3-D standards and commercial Telone II were provided by Dow AgroSciences (Indianapolis, IN). Telone II consisted of 96% 1,3-D (52% (Z)-1,3-D and 48% (E)-1,3-D) and 4% other materials. (Z)- and (E)-1,3-D standards were 99.0-99.4%pure. Plastic film was a transparent virtually impermeable film (VIF) with 0.025 mm (1 mil) thickness (Hytibar, Klerk's Plastics, Hoogstraten, Belgium).⁵ Ellipsoidal polyethylene microplot tubs (100 cm wide, $130 \text{ cm} \log \text{ and } 60 \text{ cm} \text{ deep}) (\text{Fig } 1)^{17} \text{ that contained}$ about 550 liters of Arredondo fine sand were located on the campus of the University of Florida. Some of the microplots were mixed with yard waste compost (YWC) in 1995 to increase soil organic matter content. When this study was carried out in 2001, soil organic matter contents in these plots were still substantially larger than that in the untreated plots (Table 1).

2.2 Treatment and sampling

Prior to this study, the microplots had been individually covered with a water-resistant tarp for more than 1 year to prevent wetting by rainfall, and

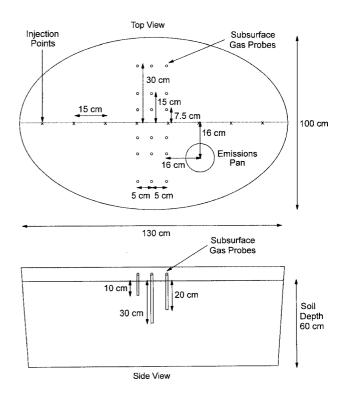


Figure 1. Schematic diagram of a microplot.

soil in the microplots was practically air-dry. Sixteen to 18 h before injection of 1,3-D, water was added to soil in some microplots to raise soil moisture to around field capacity or near water saturation. Before the injection, water in the bottom of the microplots was drained and the port was then closed. Some of the microplots were then covered with VIF. To retard 1,3-D volatilization from the edge of the microplots, the film at the edge of microplots was tucked inside the edge to about 10 cm, and the gap between the film and microplot filled with a layer of soil. 1,3-Dichloropropene in the form of Telone II was injected

Table 1. Soil-water contents and soil organic matter carbon of unamended and YWC-amended Arredondo soil in microplots

| | Gravime | Soil organic matter | | |
|---------------------------|--------------------|---------------------|--------------------|-------------------------------|
| Soil/Moisture status | 0-8 cm | 8-15 cm | 23-30 cm | carbon (%) (±SD) ^a |
| Bare soil | | | | |
| Air dry | $2.72 (\pm 1.01)$ | $3.65 (\pm 0.54)$ | $4.94 (\pm 0.74)$ | $0.37 (\pm 0.04)$ |
| Near field capacity | 6.82 (±0.41) | 8.26 (±0.74) | 12.04 (±0.62) | $0.39 (\pm 0.05)$ |
| Near water saturation | $8.67 (\pm 1.29)$ | 10.21 (±0.83) | $21.96 (\pm 4.00)$ | $0.41 (\pm 0.05)$ |
| VIF-covered soil | | | | |
| Air dry | $1.74 (\pm 0.63)$ | 3.25 (±0.11) | $4.67 (\pm 0.29)$ | $0.37 (\pm 0.04)$ |
| Near field capacity | $8.66 (\pm 0.93)$ | $9.89 (\pm 0.98)$ | 14.91 (±1.99) | $0.39 (\pm 0.05)$ |
| Near water saturation | 8.47 (±0.23) | $10.46 (\pm 0.77)$ | 20.80 (±1.08) | $0.41 (\pm 0.05)$ |
| YWC-amended soil | | | | |
| Air dry | 5.31 (±1.61) | $6.43 (\pm 1.47)$ | 8.35 (±0.21) | $0.97 (\pm 0.30)$ |
| Near field capacity | 10.05 (±0.54) | $9.05 (\pm 0.35)$ | $12.00 (\pm 0.86)$ | $1.26 (\pm 0.31)$ |
| Near water saturation | $13.79 (\pm 2.02)$ | 19.18 (±5.18) | $27.86 (\pm 2.05)$ | $1.38 (\pm 0.48)$ |
| YWC-amended VIF-covered s | oil | | | |
| Air dry | $5.30 (\pm 0.02)$ | $6.88 (\pm 0.74)$ | 10.32 (±0.38) | $0.97 (\pm 0.30)$ |
| Near field capacity | 8.87 (±0.36) | 10.68 (±0.43) | 13.55 (±1.10) | 1.26 (±0.31) |
| Near water saturation | 12.32 (±0.17) | 17.22 (±0.70) | 28.24 (±3.41) | 1.38 (±0.48) |

 $^{^{}a} n = 6.$

into the soil at 30 cm depth at eight points 15 cm apart along the center line in microplots (Fig 1) using a 40cm-long stainless steel needle and a gas-tight glass syringe at an amount of 1.21 g (1 ml) per injection point. A total amount of 9.68 g Telone II, equivalent to 200 kg ha⁻¹ (18 gal acre⁻¹), was injected in each microplot. Three sets of stainless steel soil pore gas probes (10, 20 and 30 cm in length)⁷ were installed at 7.5, 15 and 30 cm from the center of both sides for sampling soil pore air. Each set consisted of six probes of the same length. A 4.7-liter stainless steel collection pan outfitted with a stainless steel bulkhead union containing a Teflon-lined septum was placed on the surface of each microplot for collection of surface air. The pan had a diameter of 24.5 cm and the center of the pan was 16 cm from the injection line and 16 cm from the 20-cm probes. Once a day for 5 days, 30 ml of soil pore air were withdrawn from the probes using plastic syringes, and the air passed through an ORBO-32 activated charcoal tube (Supelco, Bellefonte, PA). After soil pore air sampling was completed, a collection pan was placed on the surface of each microplot. At 20-min intervals for 80 min, 50 ml of surface air were withdrawn from the collection pans and the air passed through an ORBO-32 tube. At the end of the experiments, soil samples at three depths (10-12,20-22 and 30-32 cm) were collected in glass tubes for determination of (Z)- and (E)-1,3-D residues. Prior to and after the experiments, soil samples at three depths (0-8, 8-15 and 23-30 cm) were collected in plastic bags for determination of soil-water contents. ORBO-32 tubes and soil samples were kept in an ice chest and transported to the laboratory within 3h of collection. All samples, with the exception of soil samples in the plastic bags, were immediately stored in a -80 °C ultra-cold freezer and analyzed within 3 weeks. Soil samples in the plastic bags were immediately used for determination of soil-water contents.

2.3 Analysis

The (Z)- and (E)-1,3-D in the ORBO-32 activated charcoal tubes that absorbed 1,3-D from soil pore air were analyzed by headspace GC using a Perkin–Elmer Autosystem GC (Norwalk, CT) equipped with a headspace autosampler, 63 Ni electron capture detector, split-splitless injector, and Turbochrom 4 software. Analytical procedures were similar to that described by Gan et al.18 Briefly, charcoal in ORBO-32 tubes was transferred to glass vials (22 ml) for headspace GC. After adding benzyl alcohol (3 ml), (Z)- and (E)-1,3-D in the charcoal were quantified by headspace GC. The retention times for (Z)and (E)-1,3-D were 1.35 and 1.47 min, respectively. The (Z)- and (E)-1,3-D in the soil samples in the glass tubes and in the ORBO-32 charcoal tubes that absorbed 1,3-D from the surface air of the collection pots were extracted with acetone and analyzed by the Perkin-Elmer Autosystem GC equipped with an autosampler and 63Ni electron capture detector as described previously. 11 The retention times for (Z)-

and (E)-1,3-D were 4.7 and 5.0 min, respectively. The (Z)- and (E)-1,3-D in ORBO tubes were found to be stable for at least 5 weeks when stored at $-80\,^{\circ}$ C.

2.4 Isopleths of (Z)- and (E)-1,3-D

We used the geostatistical program GS+, version 5.1 (Gamma Design Software, Plainwell, MI) to construct the two-dimensional diffusion isopleths of (Z)- and (E)-1,3-D vapor concentration in subsurface soil at 0 to 30 cm depth. The sample data were entered in a spreadsheet format that contained sample collection times, sample locations as Cartesian coordinates, and sample concentrations ($\mu g m l^{-1}$). Next, a semi-variance analysis was performed to produce a variogram model. The variogram was typically based on a linear, spherical or exponential isotropic model. The model was chosen based on the residual sum squares of the error (RSS), wherein, the lower the RSS, the better the fit. Once the model had been selected, an interpolation file was generated by kriging on a uniform grid.¹⁹ Finally, drawing and combining of the contour lines was accomplished using the computer program, Surfer, version 5.0 (Golden Software, Golden, CO). Contour lines of (Z)- and (E)-1,3-D in soil profiles of 0-30 cm depth were constructed using the vapor concentrations of the two isomers in soil at three depths (10, 20 and 30 cm) with time.

3 RESULTS AND DISCUSSION 3.1 Effect of water content on distribution of

1,3-D

Table 1 shows soil-water contents of the Arredondo soil in three depths (0-8, 8-15 and 23-30 cm) in the microplots used for this study. 1,3-Dichloropropene in soil pore air of the air-dry Arredondo soil in the microplot without VIF cover (bare) diffused upward from the point of injection more rapidly than in the near-field-capacity soil (Fig 2). It was likely that the vapors of (Z)- and (E)-1,3-D in soil air of the air-dry soil had reached maximum concentrations shortly after 5h after injection, because their vapor concentrations at all three depths (10, 20 and 30 cm) had declined substantially after 29 h. This indicated that the majority of (Z)- and (E)-1,3-D had volatilized into the atmosphere or degraded or sorbed. Since (Z)- and (E)-1,3-D concentrations in soil pore air and the ratio of (Z)-1,3-D to (E)-1,3-D (Table 2) declined rapidly, this fumigant in air-dry bare soil would provide little pest control. However, vapors of (Z)- and (E)-1,3-D were not found in soil air of the soil maintained at near field capacity at all the three depths until between 5 and 29 h after injection (Fig 2). Since

(Z)-1,3-D is more volatile than (E)-1,3-D, 10 more

(Z)-1,3-D was generally found in soil pore air of the

soil maintained at air-dry and near field capacity than

(E)-1,3-D. This disparity between (Z)- and (E)-1,3-D

concentrations has also been found in soil pore air

in Hawaiian field plots.7 With the exception of small

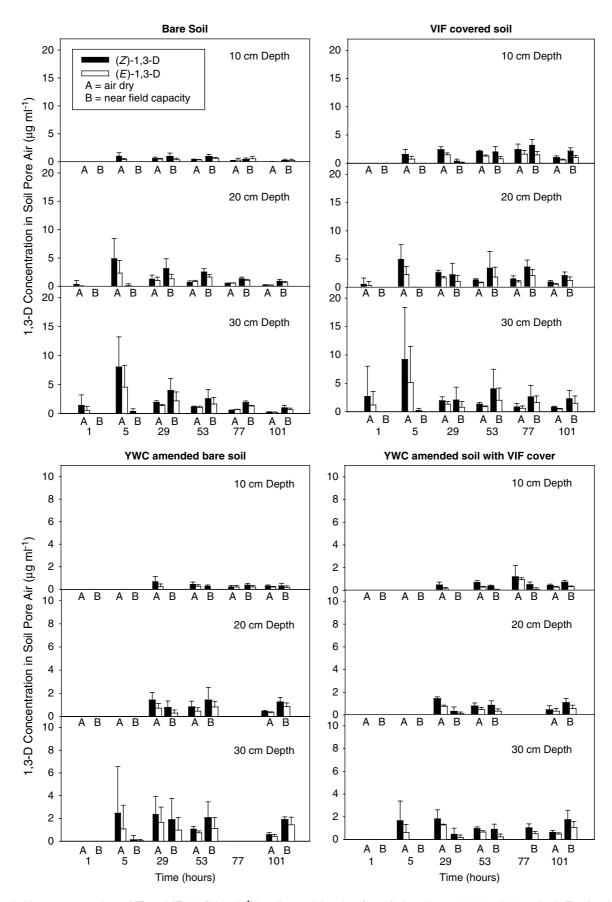


Figure 2. Vapor concentrations of (Z)- and (E)-1,3-D (μg ml⁻¹) in soil pore air in subsurface of microplots at 10, 20 and 30 cm depth. The Arredondo soil in microplots was bare, covered with VIF, bare and amended with YWC, or covered with VIF and amended with YWC. Soil moisture was maintained at air-dry or near field capacity.

amounts ($<0.40 \,\mu\mathrm{g}\,\mathrm{ml}^{-1}$) of (Z)-1,3-D found at 20 cm depth at 77 and 101 h after injection, (Z)-1,3-D vapor in the near-water-saturated Arredondo soil was not detected at all the three depths and (E)-1,3-D was never detected (data not shown). Since practically no diffusion of (Z)- and (E)-1,3-D was observed in the Arredondo soil maintained at near water saturation, application of 1,3-D would provide little pest control.

Pest-control efficacy is determined in part by the residence time of the fumigant in the soil; hence, volatilization rate from the soil surface is important. Due to contamination of unknown chemicals in the ORBO-32 charcoal tubes used for trapping (Z)- and (E)-1,3-D vapors from the bare soil at 5 h after injection, the two isomers in these tubes could not be analyzed by GC (Table 3). Since considerable amounts of (Z)- and (E)-1,3-D vapors had already diffused to 10 cm depth in the air-dry bare soil 5 h after injection (Fig 2) and their concentrations probably reached maximum shortly after 5 h, it was likely that maximal surface emissions of the two isomers would also occur shortly after 5 h, (Z)-1,3-D first

Table 2. Ratio of (*Z*)-1,3-D vapor to (*E*)-1,3-D vapor in soil pore air in subsurface of microplots at 10, 20 and 30 cm depth

| | | Ratio | Ratio of (Z)-1,3-D to (E)-1,3-D ((Z)/(E)) | | | | |
|-------------|---------------|---------|---|---------|---------------------|--|--|
| | | E | 3are | VIF | | | |
| Time (h) | Depth (cm) | Air-dry | Near field capacity | Air-dry | Near field capacity | | |
| Uname | ended soil | | | | | | |
| 5 | 10 | 2.56 | CNEa | 2.18 | CNE | | |
| | 20 | 2.09 | CNE | 2.20 | CNE | | |
| | 30 | 1.77 | CNE | 1.79 | CNE | | |
| 29 | 10 | 1.23 | 2.72 | 1.61 | 6.33 | | |
| | 20 | 1.24 | 2.36 | 1.55 | 2.20 | | |
| | 30 | 1.42 | 1.83 | 1.45 | 2.64 | | |
| 53 | 10 | 1.08 | 1.56 | 1.65 | 2.56 | | |
| | 20 | 0.80 | 1.54 | 1.65 | 1.88 | | |
| | 30 | 1.07 | 1.58 | 1.51 | 2.00 | | |
| 77 | 10 | 0.72 | 0.81 | 1.52 | 2.15 | | |
| | 20 | 0.93 | 1.26 | 1.58 | 1.71 | | |
| | 30 | 0.80 | 1.47 | 1.42 | 1.64 | | |
| 101 | 10 | CNE | 0.96 | 1.77 | 2.13 | | |
| | 20 | CNE | 1.38 | 1.76 | 1.63 | | |
| | 30 | CNE | 1.52 | 1.67 | 1.54 | | |
| YWC-a | mended s | oil | | | | | |
| 5 | 10 | CNE | CNE | CNE | CNE | | |
| | 20 | CNE | CNE | CNE | CNE | | |
| | 30 | 2.29 | 3.60 | 2.72 | CNE | | |
| 29 | 10 | 2.91 | CNE | 3.27 | CNE | | |
| | 20 | 2.00 | 2.89 | 1.88 | 2.67 | | |
| | 30 | 2.29 | 1.94 | 1.42 | 2.61 | | |
| 53 | 10 | 1.63 | CNE | 2.32 | 7.80 | | |
| | 20 | 1.84 | 1.73 | 1.63 | 2.53 | | |
| | 30 | 1.45 | 1.87 | 1.47 | 3.79 | | |
| 101 | 10 | 1.45 | 1.76 | 1.55 | 2.21 | | |
| | 20 | 1.38 | 1.50 | 1.38 | 1.90 | | |
| | 30 | 1.35 | 1.33 | 1.31 | 1.67 | | |

^a CNE = cannot be estimated.

and then the (E)-1,3-D. Surface emissions of (Z)-and (E)-1,3-D in the near-field-capacity soil initially increased with time and probably peaked just before or shortly after 53 h (Table 3). Volatilization rates of the two isomers in the soil maintained at the two water regimes markedly decreased between 53 and 77 h after injection. Surface emissions of the two isomers in the near-water-saturation soil were low and relatively stable throughout the entire experimental period. More (Z)-1,3-D isomer volatilized from the soil surface under all three water regimes than (E)-1,3-D.

Since there were greater surface emissions for (Z) isomer, less (Z)-1,3-D than (E)-1,3-D would be left as residual in the soil (Table 4). More (E)-1,3-D residues were generally found in the microplots that maintained soil moisture at air-dry and near field capacity than (Z)-1,3-D.

Table 3. Flux of (Z)- and (E)-1,3-D from soil surface of microplots at soil moisture of air dry, near field capacity or near water saturation

| | | Volatiliz | Volatilization rate of 1,3-D (g h^{-1} ha^{-1}) | | | | |
|------------------|-----|-----------|--|-----------|--------------------|--|--|
| Moisture Time | | Ва | are | VIF | | | |
| status | (h) | (Z)-1,3-D | (<i>E</i>)-1,3-D | (Z)-1,3-D | (<i>E</i>)-1,3-D | | |
| Unamended soil | | | | | | | |
| Air-dry | 5 | NDa | ND | 0 | 0 | | |
| | 29 | 184.8 | 146.6 | 12.9 | 10.7 | | |
| | 53 | 147.3 | 128.7 | 6.8 | 7.1 | | |
| | 77 | 41.3 | 33.8 | 13.0 | 12.4 | | |
| | 101 | 29.2 | 41.3 | 8.9 | 7.9 | | |
| Near field | 5 | ND | ND | 0 | 0 | | |
| capacity | 29 | 118.6 | 42.7 | 4.1 | 6.1 | | |
| | 53 | 218.0 | 119.4 | 6.1 | 6.5 | | |
| | 77 | 76.5 | 63.6 | 26.0 | 19.7 | | |
| | 101 | 39.5 | 29.0 | 21.0 | 18.2 | | |
| Near water | 5 | ND | ND | 0 | 0 | | |
| saturation | 29 | 17.1 | 10.8 | 0 | 0 | | |
| | 53 | 18.4 | 10.6 | 0 | 0 | | |
| | 77 | 30.9 | 13.0 | 0 | 0 | | |
| | 101 | 15.6 | 6.8 | 0 | 0 | | |
| YWC-amended soil | | | | | | | |
| Air-dry | 5 | 7.9 | 5.9 | 0 | 0 | | |
| | 29 | 107.1 | 33.1 | 4.2 | 0 | | |
| | 53 | 64.3 | 35.7 | 6.6 | 3.3 | | |
| | 77 | 69.1 | 40.7 | 4.2 | 3.9 | | |
| | 101 | 61.7 | 37.5 | 15.9 | 14.1 | | |
| Near field | 5 | 0 | 0 | 0 | 0 | | |
| capacity | 29 | 23.9 | 9.0 | 0 | 0 | | |
| | 53 | 121.4 | 46.9 | 0 | 0 | | |
| | 77 | 114.5 | 47.4 | 0 | 0 | | |
| | 101 | 63.0 | 33.9 | 31.0 | 20.4 | | |
| Near water | 5 | 0 | 0 | 0 | 0 | | |
| saturation | 29 | 0 | 0 | 0 | 0 | | |
| | 53 | 0 | 0 | 0 | 0 | | |
| | 77 | 0 | 0 | 0 | 0 | | |
| | 101 | 0 | 0 | 0 | 0 | | |

a ND = no data.

Table 4. Residues of (Z)- and (E)-1,3-D in subsurface of microplots at the end of 101 h experiments

| Moisture status | | | 1,3-D concentration ($\mu g g^{-1}$) | | | | |
|-----------------------|------------|-----------|--|-----------|--------------------|--|--|
| | Depth (cm) | Ba | are | V | /IF | | |
| | | (Z)-1,3-D | (<i>E</i>)-1,3-D | (Z)-1,3-D | (<i>E</i>)-1,3-D | | |
| Unamended soil | | | | | | | |
| Air-dry | 10-12 | 0.008 | 0.024 | 0.061 | 0.082 | | |
| • | 20-22 | 0.015 | 0.031 | 0.072 | 0.096 | | |
| | 30-32 | 0.012 | 0.029 | 0.069 | 0.078 | | |
| Near field capacity | 10-12 | 0.093 | 0.110 | 0.063 | 0.077 | | |
| | 20-22 | 0.041 | 0.087 | 0.122 | 0.142 | | |
| | 30-32 | 0.097 | 0.175 | 0.187 | 0.259 | | |
| Near water saturation | 10-12 | 0.008 | 0.004 | 0.002 | 0.005 | | |
| | 20-22 | 0.039 | 0.033 | 0.004 | 0.006 | | |
| | 30-32 | NDa | ND | 0 | 0 | | |
| YWC-amended soil | | | | | | | |
| Air-dry | 10-12 | 0.073 | 0.125 | 0.223 | 0.203 | | |
| | 20-22 | 0.054 | 0.106 | 0.166 | 0.215 | | |
| | 30-32 | 0.140 | 0.344 | 0.367 | 0.484 | | |
| Near field capacity | 10-12 | 0.041 | 0.070 | 0.067 | 0.077 | | |
| | 20-22 | 0.067 | 0.119 | 0.131 | 0.169 | | |
| | 30-32 | 0.484 | 0.847 | 0.484 | 0.785 | | |
| Near water saturation | 10-12 | 0 | 0 | 0 | 0 | | |
| | 20-22 | 0 | 0.001 | 0 | 0 | | |
| | 30-32 | 0.027 | 0 | 0.729 | 0.503 | | |

a ND = no data.

3.2 Effect of organic matter on distribution of 1,3-D

Unlike the unamended Arredondo soil, (Z)- and (E)-1,3-D in the YWC-amended soil maintained at air-dry and near field capacity, especially the near-fieldcapacity soil, diffused upward more slowly (Fig 2). The (Z)- and (E)-1,3-D vapor concentrations in soil pore air in the amended soil maintained at near field capacity generally were smaller than that in the unamended soil. Average soil organic matter carbon contents of the YWC-amended soil in the three depths were 2.6 to 3.4 times greater than in the corresponding depths of the unamended soil (Table 1). Average percentage values of soil organic matter carbon for both unamended and amended soils increased with soil depth, although the differences were not statistically significant. Soil having high organic matter content has higher sorption capacity for pesticides than that having low organic matter content.²⁰ Besides higher sorption capacity, organicmatter-amended soil may promote biodegradation of 1,3-D. 16 As with the unamended soil, (Z)- and (E)-1,3-D in the air-dry amended soil diffused more rapidly than in the near-field-capacity amended soil, but more slowly than in the unamended soil. More (Z)isomer was found in soil pore air in the amended soil maintained at air-dry and near field capacity than the (E) isomer (Table 2). Vapors of (Z)- and (E)-1,3-D were never detected in the amended soil maintained at near water saturation (data not shown).

Since organic matter of YWC retarded upward diffusion of (Z)- and (E)-1,3-D in the YWC-amended

Arredondo soil, surface emissions were also reduced when compared with unamended Arredondo soil (Table 3). Surface emissions of (Z)- and (E)-1,3-D in the YWC-amended Arredondo soil in microplots were not observed in the near-water-saturated soil during the entire experimental period (Table 3).

Since volatilization loss from the YWC-amended soil was less than from the unamended soil, larger amounts of (Z)- and (E)-1,3-D residues generally remained in the YWC-amended soil than in the corresponding unamended soil (Table 4). Amendment with YWC retarded 1,3-D diffusion and lowered 1,3-D concentration in soil pore air, thus pesticidal efficacy would be expected to be poor.

3.3 Effect of plastic cover on distribution of 1,3-D

With VIF cover on the Arredondo soil surface of microplots, (Z)- and (E)-1,3-D vapors in the unamended soil at soil-water content near field capacity diffused slowly and did not move upward to the 10 cm depth until about 29 h after injection (Fig 2). Since (Z)-1,3-D is more volatile than (E)-1,3-D, a small amount of (Z)-1,3-D had moved upward to 20 cm depth after 5 h, but none of the (E)-1,3-D. Overall, the soil with VIF cover and maintained at near field capacity retained larger (Z)- and (E)-1,3-D vapor concentrations which distributed more uniformly in soil pore air at all the three depths than the same soil without the plastic cover. In the air-dry soil with VIF cover, upward movement of (Z)- and (E)-1,3-D was rapid, but not as rapid as in the bare soil (Fig 2).

Neither (Z)-1,3-D nor (E)-1,3-D during the entire experimental period (101 h) was ever detected in the Arredondo soil with VIF cover that was maintained at near water saturation (data not shown). As expected, upward movement of (Z)- and (E)-1,3-D vapors was more rapid in the air-dry soil with VIF cover than in the near field capacity soil with the same cover, but not as fast as the air-dry bare amended soil.

Generally, more (Z)-1,3-D vapor was found in the soil pore air than (E)-1,3-D in all microplots with or without YWC amendment and with or without plastic cover as shown by the ratio of (Z)-1,3-D to (E)-1,3-D being generally larger than 1 (Table 2). The (Z) isomer, not the (E) isomer, is considered to have the main nematicidal activity. ^{21,22} Based on the diffusion of (Z)-1,3-D, its concentrations in soil pore air, and the ratio of (Z)-1,3-D to (E)-1,3-D, this fumigant in the Arredondo soil with VIF cover and maintained at near field capacity should provide better pesticidal efficacy than without the cover and in air-dry soil with VIF cover.

The influence of VIF cover on upward and horizontal diffusion of the chemical with time was illustrated by isopleths of (Z)-1,3-D in the Arredondo soil in microplots in which soil-water content was maintained at near field capacity (Fig 3). Virtually impermeable film retarded diffusion and retained (Z)-1,3-D in the soil profiles better than without the film cover, and thereby emissions of the chemical into the atmosphere should be reduced. This observation is in accord with the findings of Wang and Yates.²³ Figure 3 also shows maximum observed diffusion of (Z)-1,3-D in microplots under two water regimes (airdry and near field capacity), with or without VIF cover, and with or without YWC amendment. Since the (Z) isomer is the main chemical responsible for killing soil nematodes,^{21,22} we show only isopleths of (Z)-1,3-D. Isopleths of (E)-1,3-D were similar to that of (Z)-1,3-D, except that concentrations of its contour lines were lower. Since no diffusion was observed in the microplots that had soil-water content of near saturation, contour lines for (Z)- and (E)-1,3-D could not be constructed. As expected, (Z)-1,3-D in the air-dry Arredondo soil in the two microplots with and without VIF cover diffused rapidly and maximum observed diffusion was 5h after injection. In contrast, (Z)-1,3-D diffusion in the YWC-amended soil maintained at soil-water content of near field capacity was slow, especially with VIF cover.

Surface emissions of (*Z*)- and (*E*)-1,3-D were greatly retarded under VIF from the unamended and YWC-amended Arredondo soil in the three water regimes (Table 3). Surface emissions of the two isomers from the near-water-saturated soil with VIF cover and with or without YWC amendment were not observed during the entire experimental period of 101 h. In comparison, surface emissions were not observed from the two unamended microplots with lesser soil-water contents (air-dry and near field capacity) and VIF cover until 29 h after injection.

Overall surface emissions from the two unamended microplots with VIF cover were low and relatively stable between 29 and 101 h. The addition of YWC amendment in conjunction with the VIF cover not only reduced, but also delayed the emissions of 1,3-D from the microplots with lesser soil-water contents. In the near-field-capacity YWC-amended soil with VIF cover, surface emissions of (Z)- and (E)-1,3-D were not observed until 101 h after injection. With VIF cover to the air-dry YWC amended soil, surface emissions for (E)-1,3-D were delayed until 53 h after injection, and surface emissions of the two isomers were lower between 29 and 77 h than from the same soil without VIF cover.

Residues of (Z)- and (E)-1,3-D in unamended and YWC-amended soil maintained at air-dry and near field capacity and with VIF cover were generally greater than in the corresponding soil without VIF cover (Table 4). As with the Arredondo soil without VIF cover, levels of (E)-1,3-D residues were generally larger than those of the (Z) isomer. Due to poor diffusion of (Z)- and (E)-1,3-D in the near-water-saturated Arredondo soil, the residues of the two isomers in the near-water-saturated soil with or without YWC amendment and with VIF cover were either none or in trace amounts, with the exception of the YWC-amended soil at 30–32 cm depth where $0.729 \,\mu g \, g^{-1}$ of (Z)-1,3-D and $0.503 \,\mu g \, g^{-1}$ of (E)-1,3-D were detected.

4 CONCLUSIONS

This study used microplots to demonstrate that soil moisture, soil organic matter and plastic tarp could have great influence on diffusion and emissions of the volatile fumigant 1,3-D in soil. Since the volatilization flux of (Z)- and (E)-1,3-D from the near water saturated soil in microplots with or without VIF cover was very low, contamination of the two isomers to surface air should be minimal. However, upward diffusion of the two isomers in the nearwater-saturated soil was also negligible, the fumigant likely would not provide any meaningful pest control. Application of 1,3-D to air-dry soil also would not provide adequate pest control either, since (Z)- and (E)-1,3-D rapidly volatilized into the atmosphere, resulting in rapid depletion of the two isomers in soil pore air in shallow subsurface. Application of 1,3-D to near-field-capacity soil would provide better pest control than either of the other two water regimes.

Pest-control efficacy would be lowered by incorporation of YWC to the Arredondo soil since higher organic matter reduced concentrations of (Z)- and (E)-1,3-D in soil pore air. Higher application rate of the fumigant would be required for effective pest control in soil with high organic matter content.

The use of VIF cover retarded 1,3-D emissions significantly and provided good uniform distribution of 1,3-D in the root zone. Efficacy of the fumigant would be expected to be increased regardless of soil

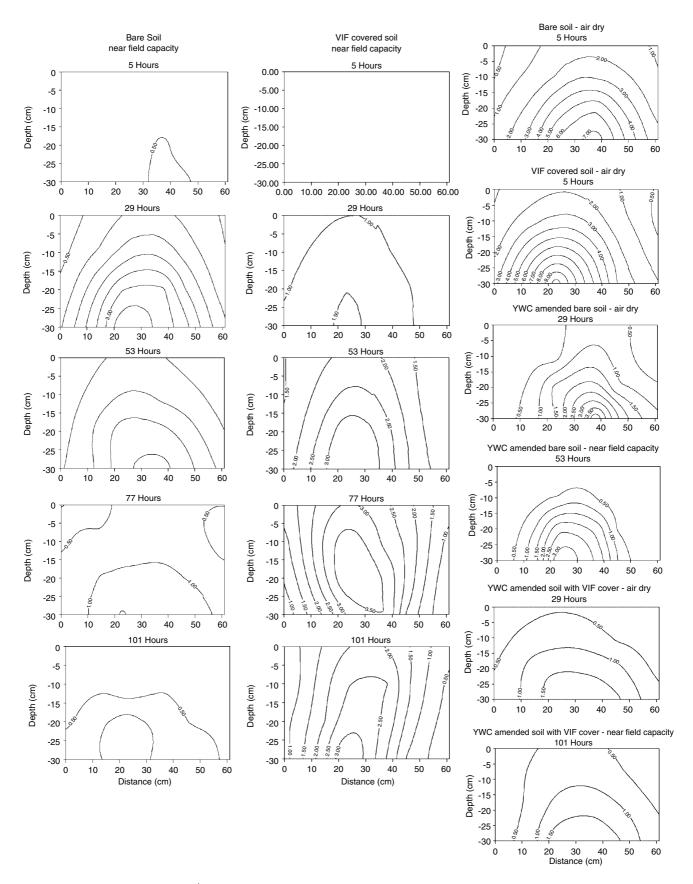


Figure 3. Isopleths of (Z)-1,3-D (μ g ml⁻¹) in the Arredondo soil profiles in microplots. Left panel: contour lines of (Z)-1,3-D diffusion in the bare soil kept at near field capacity with time; middle panel: contour lines of (Z)-1,3-D diffusion in the VIF covered soil maintained at near field capacity with time; and right panel: maximum observed (Z)-1,3-D diffusion in the bare air-dry soil (5 h), in the air-dry soil covered with VIF (5 h), in bare air-dry soil amended with YWC (29 h), in the near-field-capacity soil amended with YWC (53 h), in the air-dry YWC amended soil with VIF cover (29 h), and in the near-field-capacity YWC-amended soil with VIF cover (101 h). Numbers shown in the contour lines are vapor concentrations (μ g ml⁻¹) of (Z)-1,3-D.

water or soil organic matter content if VIF cover were utilized.

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